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WASTEWATER DENITRIFICATION: COMBINED WITH CARBON ADSORPTION OR CONDUCTED IN SAND MEDIA

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SUMMARY

Efficient denitrification (85 percent removal) of secondary effluent was promoted in small scale carbon and sand columns containing media having a mean particle diameter of 0.9 mm, at detention times of less than 10 minutes, by the addition of methanol to the column influent. Denitrification was initiated in the carbon or sand within five days after commencing methanol feeding and was not adversely affected by backwashing. As a result of these findings, and in an effort to capitalize on significant economies that may be achieved by combining denitrification with carbon adsorption, a large scale study was conducted in a four stage, fixed bed, 0.3 mgd (1,140 cu m/day), granular activated carbon pilot plant to determine the efficiency of denitrification and its effect on column operation, COD removal efficiency, and carbon regeneration.

Methanol and supplementary nitrate were added to secondary effluent during two carbon column adsorption sequences to obtain average concentrations of 25.8 and 21.8 mg/l (NO_3-N). Results showed removals of 80 and 92 percent respectively with most of the denitrification occurring in the first stage (10 minute detention time) and 3 to 4 mg/l (NO_3-N) being removed, without methanol, in the subsequent stages. The equation which best fits the data, and which can be used to approximate methanol requirements, is:

$$Q_T = 1.9\ (NO_3\text{-}N) + 1.1\ (DO)$$ where

Q_T = Methanol required in mg/l

(NO_3-N) = Nitrate Nitrogen removed in mg/l

DO = dissolved oxygen removed in mg/l

Denitrification in the four-stage column showed no significant impairment of the carbon's ability to remove COD in either adsorption sequence. COD removals of 72 percent in the first sequence and 66 percent in the second were in the range of typical of data developed during the four years prior to initiating denitrification studies in the column.

High head-losses occurred in the first stage and were caused by increased biological growth. This made twice-daily backwashing necessary and, even with this frequency, headlosses averaged 30 to 50 psi (2.1 to 3.5 kg/sq cm) after less than 12 hours of operation. The biological growths also caused difficulties with dewatering the carbon and conveying into the regeneration furnace. However, once the carbon entered the furnace it regenerated normally.

The combined removal of (NO_3-N) and organic material in an activated carbon column was shown to be a feasible process costing $111 per mil gal ($29/1000 cu m). Where removal of organics are not required, denitrification using sand media can be employed at an estimated cost of $61 per mil gal ($16/1000 cu m).

INTRODUCTION

The Water Quality Office of the Environment Protection Agency and the Sanitation Districts of Los Angeles County, through a contractual agreement, operate an advanced waste treatment research facility on the grounds of the Pomona Water Renovation Plant in Pomona, California. The overall objective at Pomona is the development of the minimum cost technology capable of renovating wastewater. In order to attain this objective, the most promising available treatment processes are being field tested and evaluated on a pilot plant scale.

The removal of residual dissolved and suspended organic matter from municipal waste water treatment plant effluents is a necessary step if this water is to be reused. It has been demonstrated at Pomona, with four years of operating data from an 0.3 mgd (1,140 cu m/day), four-stage, fixed bed, granular activated carbon pilot plant complete with thermal regeneration facilities, that the use of a carbon column is a feasible process for accomplishing this removal. The results are reported elsewhere by English, et al (1).

During the demonstration of the activated carbon process, it was observed that a biological flora, functioning within the carbon column, was responsible for a reduction in both dissolved oxygen and nitrate in the secondary effluent. However, the data indicated that nitrate removals were consistently limited to 2 to 3 mg/l (NO_3-N) after passage through the four-stage system with a total empty-bed contact time of 40 minutes. Since removal of nitrogen from municipal wastewater treatment plant effluents is also a necessary and costly

step for some reuse applications, the observation of nitrate removal in the carbon column was significant and warranted further study with the following objectives:

1. Enhancing the biological system present on the carbon and improving its denitrifying capability;
2. Comparing any advantages of granular carbon over similar size inert sand media;
3. Operating single and four-stage 0.3 mgd (1,140 cu m/day) pilot plant carbon columns as nitrate removal systems to demonstrate the feasibility of this process and to determine its effect on the removal of organic matter and the handling and regeneration characteristics of the carbon.

Significant economies could be achieved in nitrogen removal if denitrification can be combined with an activated carbon system.

PRELIMINARY EVALUATION

The evaluation of columnar denitrification was INITIATED on a small scale with the intention of applying gained information to additional denitrification studies in the 0.3 mgd (1,140 cu m/day) four-stage carbon pilot plant.

Since denitrification is, by itself, of significant importance, its use is not confined to carbon column operation and would be applicable to column design using media other than carbon to provide surface area. Many applications exist for denitrification that do not require the reduction of dissolved organic material to very low levels. For this reason, a parallel study using 2 in. (5.1 cm) columns was conducted to compare the nitrate removal efficiencies in both granular carbon and sand media.

Unfiltered secondary effluent from the Pomona Water Renovation Plant, supplemented with potassium nitrate to increase the nitrate level to about 20 mg/l

(NO_3-N), was fed downflow to the columns at 7 gpm/ft^2(285 l/min/sq m). Each column was made up of four 5 ft (1.52 m) stages, and samples were taken at empty bed contact times of 5-1/2, 11, 16-1/2, and 22 minutes.

The carbon used was supplied by the Calgon Company and is similar to the production grade Filtrasorb 400 granular carbon, except it is a 16 x 40 mesh size. The sand was No. 16 with a size distribution similar to that of the carbon. Their respective mean particle diameters are: carbon, 0.88 mm, and sand, 0.97 mm.

Limited denitrification was noted when applying secondary effluent with a varying concentration of nitrate to the sand and carbon columns. Only 3 to 5 mg/l (NO_3-N) removal was possible, even at high nitrate concentrations (25 mg/l NO_3-N). Since the secondary effluent was relatively biologically stable--that is, it had a BOD of only 3 to 5 mg/l--it appeared that a carbon source, which is necessary to provide the energy for the biological reduction of the nitrate ion, was in limited supply and consequently inhibited the reaction. In order to overcome this deficiency, a soluble, readily available carbon source was tried. Methanol was selected, based on its relatively low cost per pound of COD available (2.7¢) (6.0¢/kg), ease of handling, and the ability of denitrifying organisms to use it for energy, according to the following reaction:

$$5\ CH_3OH + 6\ NO_3^- \longrightarrow 5\ CO_2 + 3\ N_2 + 7\ H_2O + 6\ OH^-$$

In this reaction, 5 moles of methanol are required to reduce 6 moles of nitrate to elemental nitrogen. This is equivalent to 1.9 mg of methanol for each mg of NO_3-N reduced to nitrogen gas.

The addition of methanol to the column influent did indeed enhance denitrification. Nitrate, nitrite, and dissolved COD (filtered with a 0.45 micron membrane and used as an indirect measure of methanol present) were routinely determined and showed that, on the average, denitrification was completed in less

than 5-1/2 minutes. This data is presented in Figure 1 and represents an average of data obtained from the analyses of 35 samples. There is little difference in the performance of the carbon and sand media.

Measurement of ammonia and organic nitrogen were made and did not significantly change in the denitrification process. Ammonia and organic nitrogen concentrations averaged 12 mg/l and 1.6 mg/l, respectively in both the influent and effluent.

The influent dissolved oxygen concentration was consistently less than 1 mg/l and averaged 0.6 mg/l. No dissolved oxygen was present in the column effluents.

The influent temperature varied from 18° to 24° C, with an average of 21° C during the study.

Physical filtration of suspended material in the secondary effluent and the increased production of biological cell material due to denitrification increased headlosses and made backwashing of the first stage columns mandatory on at least a daily or more frequent basis. The backwashing did not appear to interfere with the denitrification process since the majority of samples were taken about 30 minutes after backwashing.

In order to confirm denitrification results using sand media at a larger scale, two commercially available pressure sand filters were operated in series, with each containing 3.3 ft^3 (0.093 cu m) of No. 16 sand (0.97mm). Operating at 5.5 gpm (0.35 l/sec) provided a total empty bed detention time of nine minutes and a hydraulic application rate of 2.5 gpm/ft^2 (102 l/min/sq m). Methanol was added to the filter influent and the addition of potassium nitrate was necessary in order to increase the nitrate level in the secondary effluent. Backwashing of both filters was performed on a daily basis, at 15 gpm/ft^2 (610 l/min/sq m), and required about 700 gal (2.65 cu m), or 9% of the flow, per

backwash to remove solids and to restore the sand beds to an operable pressure loss.

Data tabulated from results of nitrate, nitrite, and dissolved COD (filtered with a 0.45 micron membrane and used as an indirect measure of methanol) analyses for samples at 4.5 and 9 minute detention times, taken over a three-month period, were averaged and are presented in Figure 2. As previously observed in the 2 in. (5.1 cm) column studies, no significant change in the concentration of ammonia and organic nitrogen occurred during the pressure filter studies due to the denitrification process. The influent dissolved oxygen level was consistently about 1.1 mg/l and the effluent was zero.

An attempt was made to maintain a methanol (as COD) to nitrate ratio of 4 to 1, to insure an adequate organic carbon source to complete the denitrification reaction. It is evident from the dissolved COD data in Figure 2 that sufficient methanol was available. However, on the average, not all the nitrate was removed, even in the presence of adequate methanol. Nearly 100% removal occurred at some periods and not at others. An average of 83% reduction was indicated in 9 minutes' empty bed contact time in the sand filters.

CARBON PILOT PLANT STUDIES

PILOT PLANT DESCRIPTION

As a result of the information gained from the small column and pressure filter studies, which indicated that efficient denitrification was feasible when using methanol and employing carbon or sand as media, studies at the pilot plant scale were warranted. Large scale verification of denitrification results, the detailing of operational parameters, and determining the feasibility of combining this process with carbon adsorption in the 0.3 mgd (1,140 cu m/day) carbon pilot plant were the next objectives of the program.

The pilot plant components include five carbon contactors, influent and product water storage tanks, a carbon dewatering bin, a quench tank, and a regeneration furnace, all mounted on a concrete slab with related piping, pumps and controls. A photograph of the carbon pilot plant is presented in Figure 3 and a schematic flow diagram for the pilot plant is shown in Figure 4.

The secondary effluent is directed to the storage tank from where it is pumped into the carbon columns. During denitrification studies methanol was injected with a metering pump into the suction side of the column feed pump at flows from 20 to 50 ml/min. The methanol used was 99% purity and purchased in 55-gallon (190 l) drums.

The pilot plant is composed of two columns, a single stage and a four stage; each of the stages or contactors is identical in design and contains 6,700 pounds (3040 kg) of 16 x 40 mesh granular activated carbon having characteristics as shown in Table I. The contactors are 6 ft (1.8 m) in diameter, have an overall height of 16 ft (4.9 m), and are designed for a working pressure of 50 psi (3.5 kg/sq cm). The detailed design of a typical contactor is shown in Figure 5. The carbon bed is supported by a Neva-Clog screen, an expanded metal backing, and a series of concentric annular rings which are an integral part of the contactors for structural support. The screen is comprised of two layers of stainless steel perforated with 1/32 in. (0.08 cm) diameter holes and spot-welded together with holes off-set from each other.

The liquid enters at the top from an annular ring through twenty 1 in. (2.5 cm) holes around the circumference of each contactor. This ring is also used to remove liquid during backwashing. A distance of 3-1/2 ft (1.1 m) between the entrance ring and the top of the carbon bed provides room for a 35 percent bed expansion during backwashing.

Backwashing is required on a daily basis and is normally accomplished at maximum rates of 200 gpm (12.6 l/sec) with a total of 5,000 to 8,000 gal (18.9 to 30.3 cu m) of secondary effluent used per backwash. This requires one hour to complete. The surface spray is operated at about 50 to 75 gpm (3.2 to 4.7 l/sec).

The single stage column was designed to provide supplementary data to that obtained from the main four-stage column pilot plant. It is operated at 200 gpm (12.6 l/sec), or a hydraulic loading of 7 gpm/ft^2 (285 l/min/sq m), which results in an empty bed detention time of 10 minutes. The water leaves the column and is discharged to the nearby San Jose Creek after chlorination.

The four-stage column also operates at 200 gpm (12.6 l/sec) and has an empty bed detention time of 40 minutes with the secondary effluent passing, in series, through each of the stages and thence to the product water storage tank with overflow entering the creek. As the carbon becomes exhausted, the level of organic matter in the effluent increases and, when it reaches a COD of 12 mg/l, the first stage is removed from service and the carbon is transferred as a slurry into the dewatering bin. The carbon, with a 40 percent moisture content, is conveyed into the multiple hearth furnace where it is regenerated at 1700°F (990°C).

The furnace is a 30-in. (76 cm) ID, vertical, refractory-lined, 6 hearth unit, complete with air pollution control equipment. It is natural gas fired and steam is added to enhance the regeneration. Carbon leaves the furnace at 90 lbs/hr (41 kg/hr) and is discharged, under water, into the quench tank. After quenching, the regenerated carbon is returned to service as the fourth-stage of the column, and through valving, the other stages are moved forward one position, thus approaching a countercurrent flow of carbon and water.

SINGLE STAGE COLUMN PERFORMANCE

Denitrification studies were initiated in the single stage column which was not part of the main four-stage column, but identical in design. This allowed testing without interfering with the routine operation of the main carbon pilot plant. Also, a parallel column, namely, the first stage of the four-stage column, was available as a control with which nitrate removal without methanol addition could be observed in a parallel operation.

Samples of column influent, before and after methanol addition, and the column effluent were taken on a routine basis. The samples were usually two-hour composites, taken during the day by means of an automatic timer and solenoid system that directed samples into refrigerated half-gallon (1.9 l) bottles. Samples were analyzed for dissolved COD (as an indirect measure of methanol), nitrate, nitrite, ammonia and turbidity. Dissolved oxygen and temperature measurements were made routinely on a grab sample basis.

Normally, the nitrate level in the secondary effluent is 7 mg/l (NO_3-N), but during this study nitrification was increased in the activated sludge plant by the addition of more air and an increase in the cell residence time to obtain an average nitrate concentration of 15 mg/l (NO_3-N). By almost totally nitrifying the effluent, no supplementary nitrate addition was necessary.

Data showing the relationship between the levels of methanol (measured indirectly as dissolved COD), nitrate, and nitrite in the column influent and effluent for slightly over a five month period are presented in Figure 6. Data from the parallel first stage (used as the control) of the four-stage column not receiving methanol are also included for comparison purposes.

The carbon was out of service between the 16th and 23rd days for regeneration. This was necessary to complete the previously planned carbon adsorption program, and after regeneration, methanol was again added to the

column influent immediately on start-up. Efficient denitrification occurred within 2 to 5 days of restarting the column.

Variations in the methanol feed occurred throughout the study and are represented in Figure 6 by the influent dissolved COD which is composed of COD due to methanol and COD due to secondary effluent. Variations in the nitrate concentration in the secondary effluent are also evident. Possible variations in methanol metering rates were anticipated and this was the primary reason for using dissolved COD as the parameter for determing the quantity of methanol added, rather than assuming a constant flow rate of methanol. Some variation in the influent dissolved COD is also due to that normally occurring in the secondary effluent.

Methanol leaked through the column when a decrease in influent nitrate occurred. Without a readily available electron acceptor such as dissolved oxygen or nitrate, all the methanol was not biologically metabolized at the detention times studied. The presence of nitrate and nitrite in the column effluent periodically occurs even in the presence of adequate methanol. The conversion of nitrate to nitrite and the latter's presence in the effluent is particularly evident at times during the first three months of the study.

Since dissolved oxygen serves as an electron acceptor and affects the methanol usage, some methanol is expended in dissolved oxygen removal and is not available for denitrification. The dissolved oxygen was relatively constant at about 5.4 mg/l in the column influent and nearly zero in the effluent throughout the study. The water temperature ranged from 17° to 24° C, with an average of 19° C.

No significant changes in the ammonia nitrogen levels occurred between the column influent and effluent during the denitrification process. Concentrations ranged from nearly zero to 10 mg/l. Periodic organic nitrogen

determinations were made, and indicated average influent and effluent concentrations of 1.6 mg/l and 0.8 mg/l, respectively. A portion of the organic nitrogen is suspended and the difference in the influent and effluent concentrations was probably due to filtration in the carbon bed.

Routine daily backwashing and the use of surface sprays was necessary to prevent unduly high pressure loss in the carbon. Twenty to thirty percent more backwash water was used for the methanol fed carbon column than for the control column, and even the extra water did not restore the pressure loss to the same level as that in the control column. In the control column there was a 4 to 6 psi (0.3 to 0.4 kg/sq cm) drop across the clean 9 to 9.5 foot (2.7 to 2.9 m) bed of carbon, and during this study it increased to 10 to 15 psi (0.7 to 1.1 kg/sq cm) over a 24-hour period. In the methanol fed column, 8 to 10 psi (0.6 to 0.7 kg/sq cm) headlosses were recorded after backwashing and increased, on the average, to 18 to 25 psi (1.3 to 1.8 kg/sq cm) after one day of operation, with pressure losses as high as 40 psi (2.8 kg/sq cm) occurring on several occasions. These higher pressure losses were a result of biological solids accumulating in and near the top of the carbon bed, which could have resulted in channeling. Variations in the detention time in the column may have been caused by channeling conditions and could be responsible for the variation in nitrate removals.

There is no adverse effect on denitrification efficiency due to removal of large portions of the biological flora from the carbon bed during backwashing. This is evident from data shown in Figure 7, which is based on six 4-hour composite samples of column influent and effluent with normal backwashing of the column performed during the 24-hour monitoring period.

Since denitrification is a biological process, new cell material is produced, and some may occur as suspended material in the process effluent. A slight increase in the level of turbidity in the methanol fed column as compared

to that in the control column is evident from the data shown in Figure 8 and can be attributed to increased microbial cell material.

FOUR STAGE COLUMN PERFORMANCE

The four-stage main carbon column study was completed in June, 1969, after four years of operation and four carbon cycles. The denitrification process was initiated during the fifth cycle and the column continued in service as in the past, serving to remove organic materials, but now also combining this function with denitrification.

Since nitrification of the activated sludge plant effluent was erratic during the period prior to initiating this study, it was decided that more uniform data could be obtained if the column influent was supplemented with nitrate. A saturated solution of sodium nitrate was metered into the feed water line upstream of the influent pump to give the desired influent nitrate concentration. Methanol, as in the single stage column study, was also added. However, during the study, analysis of methanol was accomplished using gas chromotography techniques.

Denitrification was accomplished during two adsorption sequences, the 18th and 19th. An adsorption sequence is defined as the operational period between regeneration of the first stage which usually occurs after treating about 20 mil. gal. (75,800 cu m) of secondary effluent or about every 75 days. At this point the four-stage column effluent has reached a COD of 12 mg/l, which is the criteria dictating regeneration. Four adsorption sequences are required to complete an adsorption cycle.

Nitrate plus nitrite nitrogen, methanol, and dissolved oxygen data for both the 18th and 19th adsorption sequences are presented in Figure 9. The variation in nitrate and methanol concentrations was mainly due to feeding these materials at constant rates when changes were occurring in the flow rate

through the column due to increases in headloss caused by biological growths and filtration of suspended solids from the secondary effluent.

Nitrite nitrogen averaged 1 mg/l in the column influent and was due to the presence of nitrite in the sodium nitrate feed solution, since the secondary effluent contained only a few tenths of a mg/l. Seldom was any nitrite present in the effluent of the first stage.

Average methanol and nitrogen removal data for each stage during each sequence are shown in Figure 10. During the 18th sequence, 100% denitrification was not attempted at all times, and as a result, only 82% nitrate removal occurred during the period of methanol addition. During the 19th sequence a reduction of 100% was attempted without also causing a methanol breakthrough in the column effluent. This resulted, in an average of 92% denitrification through the column.

During the entire study the nitrate reduction in the second, third and fourth stages remained relatively constant, averaging a total of 3-1/2 to 4 mg/l (NO_3-N). This is "bonus" denitrification, since little or no methanol was available to achieve it. At the end of the 18th adsorption sequence, the methanol feed was stopped while the high influent nitrate concentration was maintained. During this period, while a large population of denitrifying organisms was established in the bed, the average nitrate reduction was 4 mg/l (NO_3-N) in the first stage.

At the beginning of the 19th adsorption sequence, methanol feed was not initiated immediately although nitrate was again added, and during this period, only about 1-1/2 mg/l (NO_3-N) was removed. This shows that the established denitrifying population accounted for the relatively high degree of denitrification occurring in the absence of methanol at the end of the 18th sequence. However, this does not necessarily mean that this degree of background denitrification occurs in the presence of methanol.

There was no methanol in the effluent of the first stage nor was dissolved oxygen present during the 18th sequence. However, during the 19th sequence there was a methanol breakthrough resulting in effluent concentrations as high as 25 mg/l. This breakthrough was caused by failure of the nitrate feed pump. Methanol breakthroughs were of concern because of the possible adverse effect on other experimental pilot plant processes using the carbon product water in research studies.

Excess methanol could have also been a problem had it caused sulfide generation in the carbon contactors in the absence of nitrate, but it did not. No odors were noticed in the product water and sulfate data averaged 83 and 80 mg/l for influent and effluent respectively.

The results of bacterial analyses are shown in Table II and represent averages from 10 sets of samples. Of particular interest are the Pseudomonas counts, which were determined using Gessard's media, since these bacteria have been identified as denitrifiers although other genera may be involved. The number of Pseudomonads in the secondary effluent drops by about half in the effluent from the first stage, and the numbers coming from the remaining three stages are very low. It must be remembered that only those bacteria in the effluent from each column are being counted and not those bacteria which are attached and stationary within each bed. Nevertheless, these data show that there are ample seed bacteria in the secondary effluent and that most of the bacteria in the column, as is already known, are established in the first stage.

Figure 11 shows data for the two adsorption sequences and includes both total and dissolved COD for the column influent and effluent from the fourth stage. Samples of influent were taken before methanol addition. During the time when methanol was detected in the column effluent, which has been described previously, the effluent COD data was not utilized because of masking of the true values by the leaking methanol.

During the 19th sequence the column was receiving secondary effluent from the Pomona Water Renovation Plant while the plant was undergoing start up operations for newly completed aeration and final clarification capacity. The column treated some of the poorest quality secondary effluent during this period that had been experienced in the previous 4 years of operation, and this accounts for the higher influent and effluent concentrations of both total and dissolved COD.

During the 19th adsorption sequence the influent total COD and dissolved COD respectively, averaged 40% and 25% higher than the corresponding values during the 18th sequence. This resulted in dissolved COD removal efficiencies of 71% during the 18th and 66% during the 19th adsorption sequence. These values along with comparable data for each sequence since beginning operation of the column are shown in Figure 12. The denitrification sequences 18 and 19 are presented to show their relationship to past column operations.

Taking into account variations in column influent COD that normally occurred between each sequence during the 4 year study, the percent dissolved COD removed during the denitrification sequences is within the range of the removal that can be expected in a carbon column that is not combining denitrification in a single process.

Suspended matter in the column effluent, as measured by turbidity, averaged 1 to 2 JTU during both denitrification sequences and compares well with the 4 year column effluent average of 1.2 JTU.

Figure 13 is a plot of weekly averages of pressure drop and influent turbidity data for each adsorption sequence. During the 18th sequence the first stage was backwashed daily which is the normal interval for backwashing, but after 45 days the daily headloss averaged 17 psi (2.6 kg/sq cm) which was almost 3 times as high as that occurring prior to instituting denitrification

studies. Prior to denitrification, daily headloss in the first stage carbon averaged 17 psi (1.2 kg/sq cm) before and 6 to 7 psi (0.4 to 0.5 kg/sq cm) after backwashing.

Twice daily backwashing was initiated during both sequences but nevertheless the pressure loss remained significantly higher than normal, with values of 50 to 60 psi (3.5 to 4.2 kg/sq cm) recorded at times. The poorer quality secondary effluent during the 19the sequence contributed to the higher pressure loss during this operational period. Normally, the turbidity in the secondary effluent averaged 8 JTU, but during the 19th sequence turbidity values in excess of 20 JTU were routinely recorded.

The quantity of backwash water (secondary effluent) averaged 15,000 gal (57 cu m) per backwash which is 6% of the daily product flow. The backwash required about 1-1/2 hours to complete in order to provide a gradual stepwise increase in flow to prevent carbon carry-over and obtain a thorough flushing of the bed. Even when using 50 percent more water per backwash than is normally used, headloss in the first stage carbon bed could not be reduced to the routine 6 to 7 psi (0.4 to 0.5 kg/sq cm) level but averaged about 12 psi (0.8 kg/sq cm).

The interval for backwashing the second stage decreased from 2 to 3 weeks to 1 week, and the third stage had to be backwashed every 3 weeks which seldom was necessary in previous carbon column operations.

The carbon in the first stage, after treating 19.6 mil gal. (74,200 cu m) of secondary effluent during the 18th sequence, was removed from service, backwashed, transferred to the dewatering bin, and regenerated. However, the behavior of the spent carbon was atypical and as a result the regeneration took an unusually long time to complete--about 115 hours compared to the normal 75 hours. The dewatered carbon fed very poorly into the furnace; bridging

occurred over and carbon caked on the screw conveyor, thereby reducing its capacity. The wet drained carbon was very sticky due to the large amount of bacterial solids and slimes remaining on the carbon. The dried spent carbon granules had a brown surface residue which appeared to be the dried bacterial mass. This type of residue had not been noticed on any other spent carbon; normally, dried spent carbon appears dull black and is similar to regenerated carbon.

Once the carbon entered the furnace, which was operated as in the past, it regenerated normally. The characteristics of the spent and regenerated carbon are shown in Table III along with carbon data from the 17th sequence, during which denitrification was not accomplished. Taking into account the normal change in carbon characteristics with regeneration both sets of data are similar.

A 10% loss of carbon occurred which was slightly higher than the average of 8-1/2% for the previous 4 year study, but was in the loss range occurring during the same period.

DISCUSSION OF RESULTS

METHANOL REQUIREMENTS

Variations in percent nitrate reductions have occurred in all phases of the denitrification studies. Almost complete denitrification was achieved at times, while during other periods, 2 to 3 mg/l (NO_3-N) was present in the column effluent when sufficient methanol was available to complete the reaction. The average percent nitrate reductions in the preliminary and pilot plant phases of the study ranged from 80 to 92 percent at levels as high as 35 mg/l (NO_3-N) in the influent and represent a significant removal of nitrate by an efficient process.

Sufficient data was obtained to develop an empirical relationship between the degree of denitrification and methanol requirement. Such a relationship can be helpful in approximating the methanol costs for column operations employing a fine grained media (large surface area) at empty bed detention times of about 10 minutes. Since the quantity of methanol required depends not only on the amount of nitrate, but also on the amount of dissolved oxygen to be removed to create the anaerobic conditions necessary for denitrification, both these materials must be taken into account. A general equation expressing the empirical relationship between these parameters is as follows:

$$Q_T = Q_1 (NO_3\text{-}N) + Q_2 (DO) \text{ where}$$

Q_T = Quantity of methanol (mg/l) utilized for denitrification and deoxygenation

$(NO_3\text{-}N)$ = Quantity of nitrate removed (mg/l)

(DO) = Quantity dissolved oxygen removed (mg/l)

Q_1 = Quantity of methanol (mg/l) utilized to remove 1 mg/l of NO_3-N

Q_2 = Quantity of methanol (mg/l) utilized to remove 1 mg/l of DO

Since similar size (0.88 to 0.97 mm mean particle diameter) granular media (carbon and sand) was used and similar contact times were employed, and dissolved COD was the common technique used as an indirect measure of methanol, the data obtained from the small scale studies and the single stage carbon column were analyzed in an effort to determine the empirical value of Q_1 and Q_2 in the above equation.

Average values of Q_T, the quantity of nitrogen removed, and the quantity of DO removed in each of the three columnar systems were obtained from the data previously presented in Figure 1, 2, and 6. From this information, the following three equations were established:

2 in. (5.1 cm) carbon column:	$33.9 = Q_1 (17.9) + Q_2 (0.6)$
0.3 mgd (1,140 cu m/day) single stage carbon column:	$26.8 = Q_1 (12.0) + Q_2 (5.4)$
Sand Filter:	$18.9 = Q_1 (9.0) + Q_2 (1.1)$

Since laboratory results showed that the COD procedure recovered only 95% of the methanol, this was taken into account in determining Q_T for each of the above equations.

Unlike the 2 in. (5.1 cm) columns in which the carbon was largely spent and removed little dissolved COD, the adsorption of dissolved COD from the secondary effluent by the carbon in the 0.3 mgd (1,140 cu m/day) single stage column had to be taken into account to determine the amount of dissolved COD due to methanol in the column effluent. Data from a previous control column not receiving methanol was used to make the corrections. This averaged 4.4 mg/l COD and was used in determining Q_T for the 0.3 mgd (1,140 cu m/day) carbon column. Dissolved COD in the secondary effluent was not removed by the sand.

By solving the above three equations in groups of two, three sets of values for Q_1 and Q_2 were determined. These were averaged and used to formulate the following equation:

$$Q_T = 1.9 (NO_3\text{-}N) + 1.2 (DO)$$

As previously stated, the data obtained from the four-stage carbon column study was not included in determining the above equation, but was handled separately because a more precise analytical technique for measuring methanol was used. By segregating the data according to the influent dissolved oxygen concentration, above 1.5 mg/l (4.5 average) and below 1.5 mg/l (0.7 average), the following equations were developed for denitrification in the first stage of the four-stage system:

$$32.7 = Q_1 (16.8) + Q_2 (0.7)$$

$$36.0 - Q_1 (16.2) + Q_2 (4.5)$$

Solving these equations simultaneously yielded the following equation:

$$Q_T = 1.9 (NO_3\text{-}N) + 1.1 (DO)$$

This is similar to that derived from the earlier studies and also represents a 10 minute empty bed detention since little or no methanol was present in the effluent from the first stage. The 3.5 to 4 mg/l "bonus" removal of nitrate nitrogen occurring in subsequent stages was not included with the above data.

The theoretical methanol requirement to reduce 1 mg/l of NO_3-N to nitrogen gas is 1.9, which agrees with the above equation. Therefore, the organic material required for biological cell synthesis, which does take place as evidence by increased biological growths, may come from other sources, such as in the secondary effluent or from the organics adsorbed in the carbon granules. Another possibility is that some of these organics may be used for denitrification and a portion of the methanol for cell synthesis; the exact mechanism is not known.

OPERATION AND COSTS

The most serious problem associated with denitrification in small media (0.9 mm mean particle diameter) is caused by increased biological cell synthesis in the carbon bed resulting in a mass of biological growths, and consequently, significant increases in headloss over that normally encountered in a carbon column operating on secondary effluent. The greater headlosses increase the frequency of backwashing which results in increased down time.

The design of the pilot plant carbon vessels, while previously satisfactory for strictly carbon adsorption applications, was not as flexible as required to handle the increased headloss in the carbon bed. Backwash velocities

were limited to about 7 gpm/ft^2 (285 l/min/sq m) due to screen design and only 35% freeboard was provided for bed expansion.

In a large plant application combining carbon adsorption and denitrification, backwashing of the first stage 3 times per day for 1/2 hour at 15 to 20 gpm/ft^2 (610 to 820 l/min/sq m) with at least 50% bed expansion would be satisfactory and allow for about a 25 psi (1.8 kg/sq cm) headloss between backwashes. Utilization of the 8 x 30 mesh carbon, which has a mean particle diameter of 1.6 mm and has similar adsorptive characteristics as the 0.9 mm carbon, would also minimize the increases in headloss. Using the above backwashing regimen, an additional cost of about $10 per mil gal ($2.6/1000 cu m) over and above the cost for carbon adsorption is estimated to account for the effect of increased headloss. Ninety percent of this estimated cost is power, backwash water, and other O & M items. The remaining 10 percent includes methanol storage and feeding equipment, and slightly larger influent pumps to compensate for down time.

The stickiness of the drained carbon and subsequent difficulties with feeding it into the furnace could have been reduced by providing a more vigorous and extensive backwash before transferring into the dewatering bin. Another possible solution to consider in plant design would be the use of a different type system to feed the carbon, such as a dewatering screw or a vibrating dewatering screen feeding directly to the furnace.

The major cost of denitrification is due to methanol which, in tank car quantities, costs 4.1¢ per pound (9.0¢/kg). The cost for methanol is shown in Table IV and was estimated using the previously mentioned empirical equation, a flow of 10 mgd (37,850 cu m/day), 5 mg/l of dissolved oxygen, and removal of 20 mg/l (NO_3-N). The cost of denitrification in carbon that is shown in Table IV is over and above the $86 per mil gal ($23/1000 cu m) estimated for

carbon adsorption alone. The cost of the combined processes would be $111 per mil gal ($29/1000 cu m).

If denitrification is the only treatment process required, then a sand system would be adequate to accomplish nitrate removal. For comparative purposes the cost for such a system is included in Table IV and essentially involves the use of parallel, single stage pressure vessels containing sand, 10 minute empty bed detention times, nitrified secondary effluent supplemented with methanol, and the previously mentioned backwashing regimen.

It is evident that economies result when combining denitrification and carbon adsorption in a single system which has been shown to be a feasible process for the removal of both nitrogen and organic materials.

REFERENCE

(1) English, J. N., et al. "Removal of Organics from Wastewater by Activated Carbon," Chem. Eng. Prog. Symposium Series, No. 107, Vol. 67, p 147, (1971).

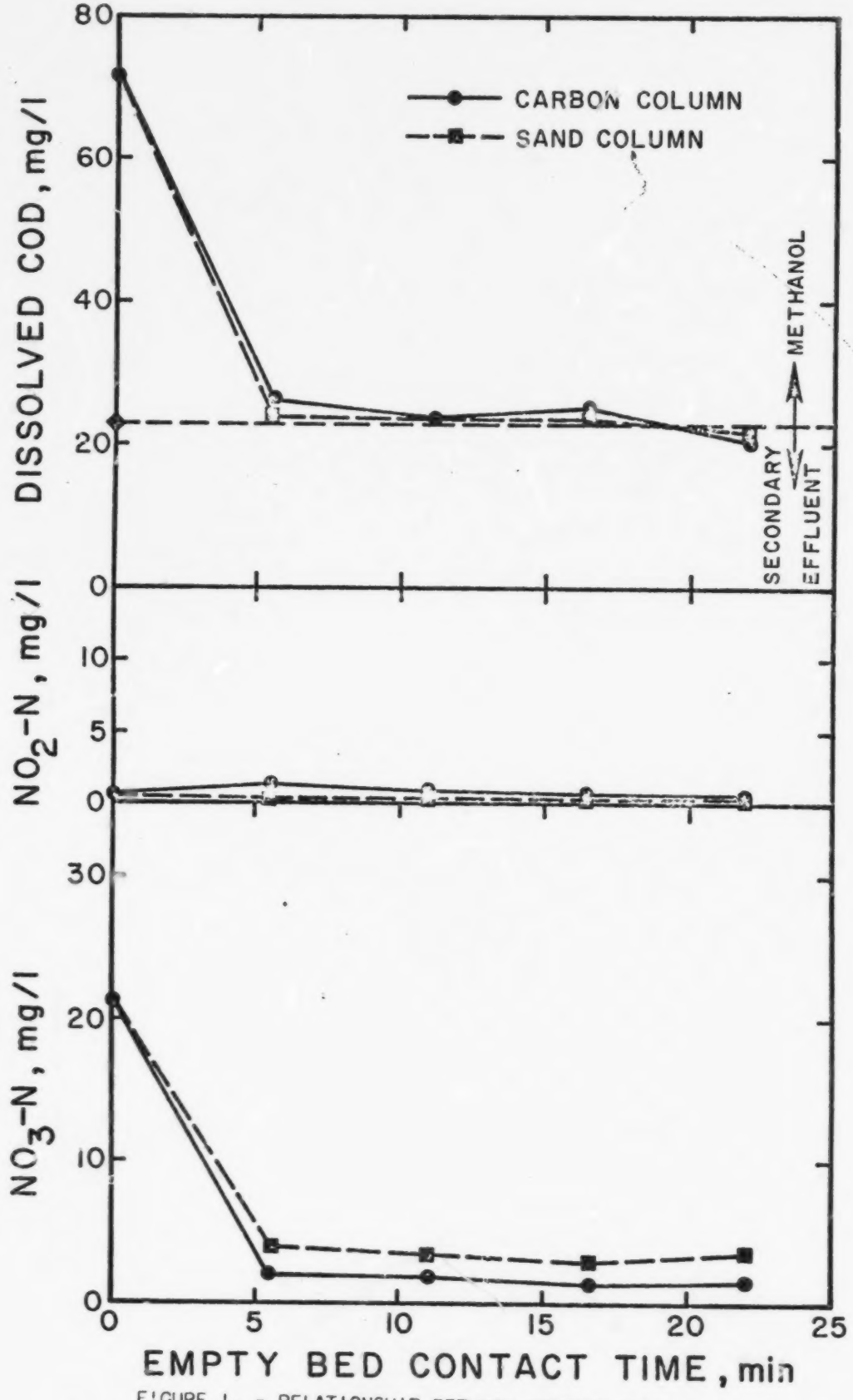

FIGURE 1. - RELATIONSHIP BETWEEN CONTACT TIME AND DENITRIFICATION IN SMALL SCALE CARBON AND SAND COLUMNS

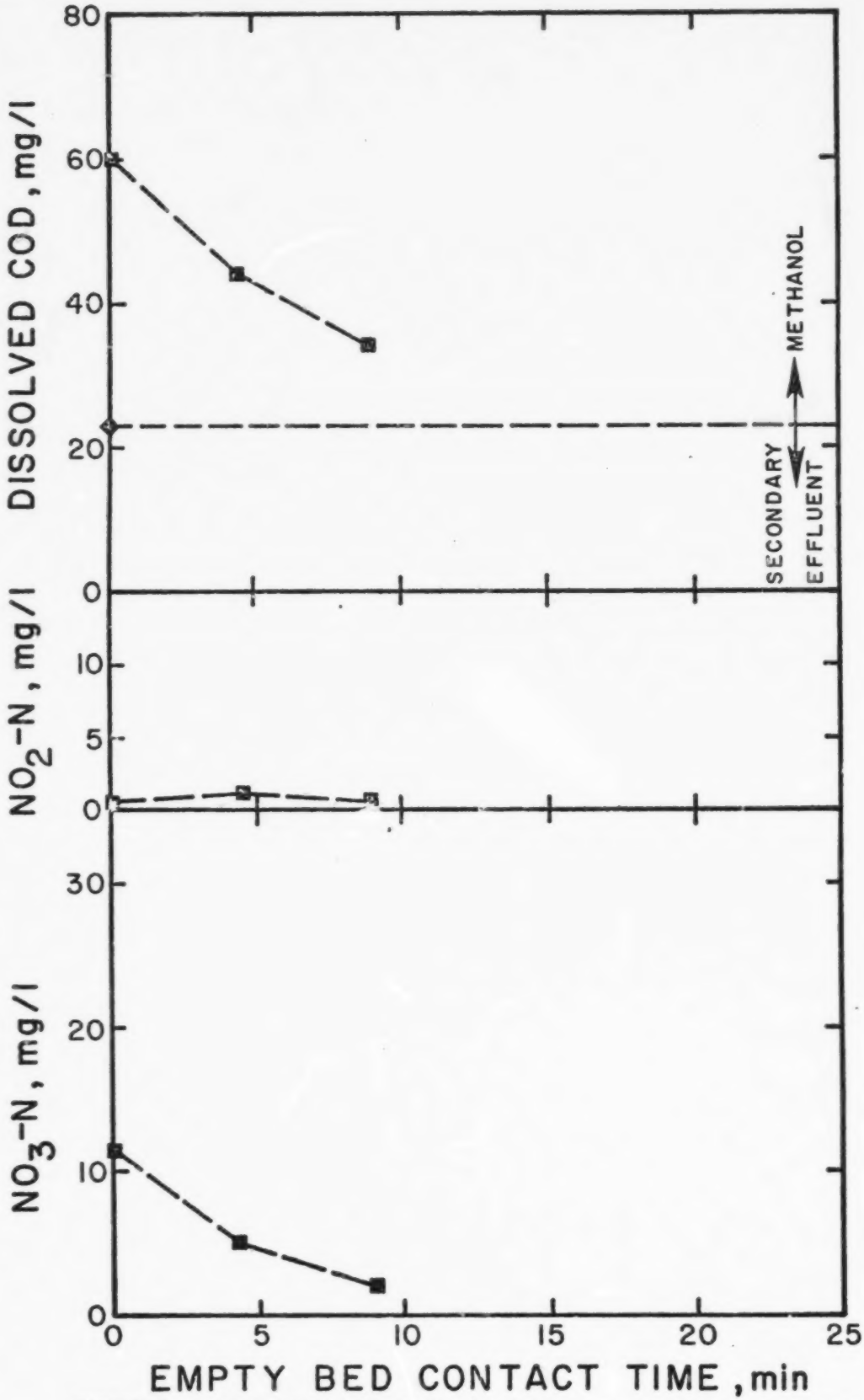

FIGURE 2. - RELATIONSHIP BETWEEN CONTACT TIME AND DENITRIFICATION IN A PRESSURE SAND FILTER

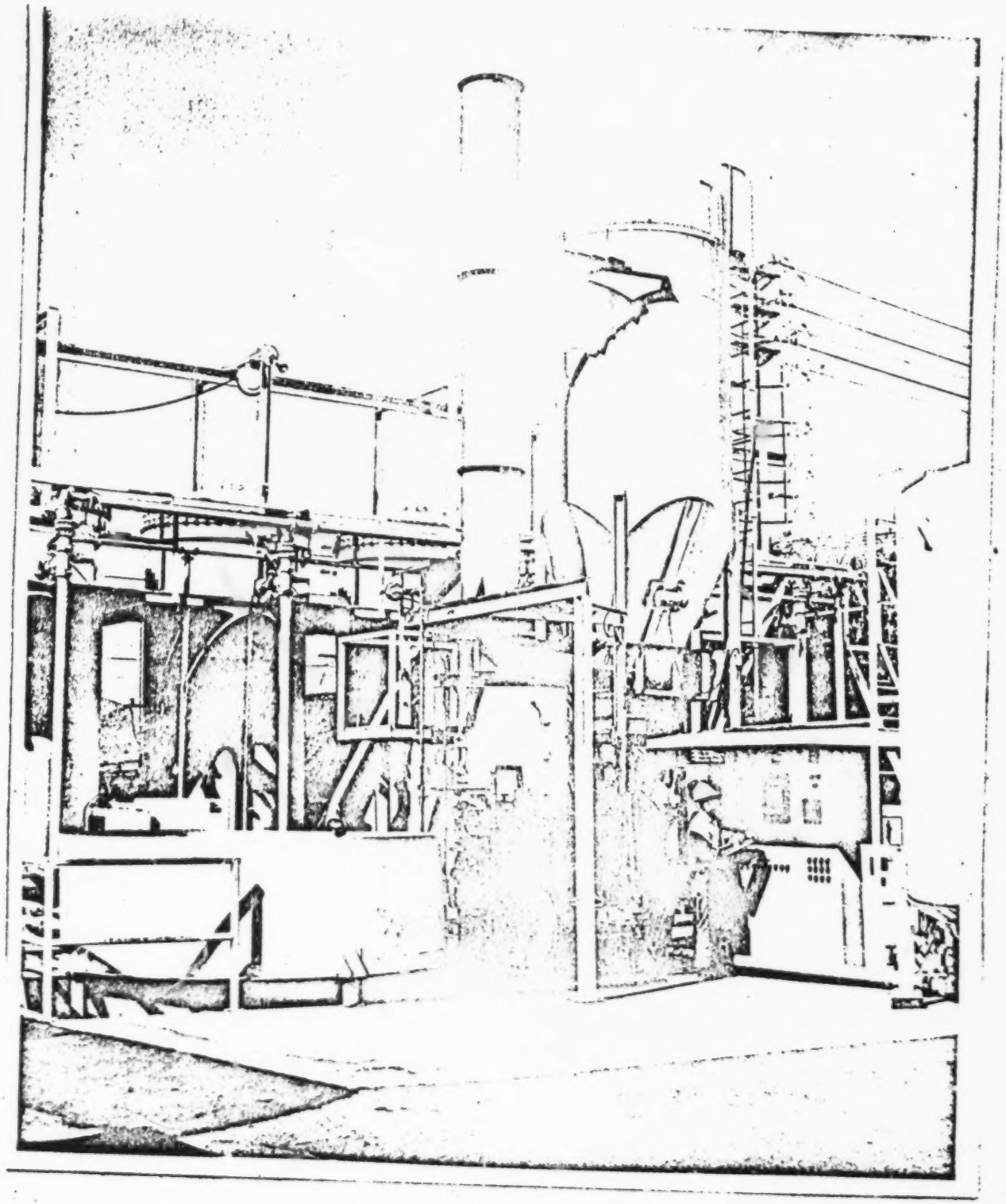

FIGURE 3. - CARBON PILOT PLANT

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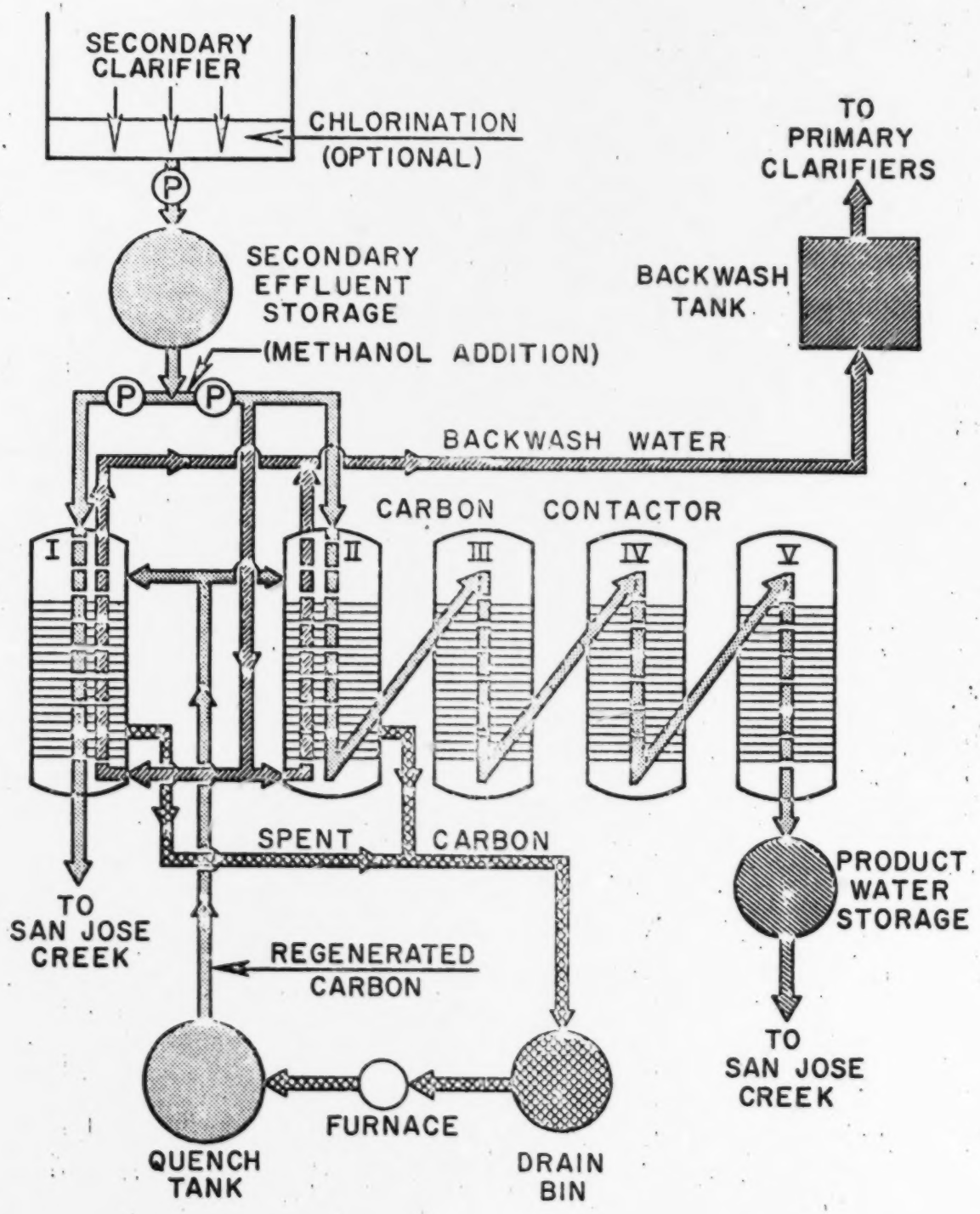

FIGURE 4. - CARBON ADSORPTION PILOT PLANT SCHEMATIC FLOW DIAGRAM

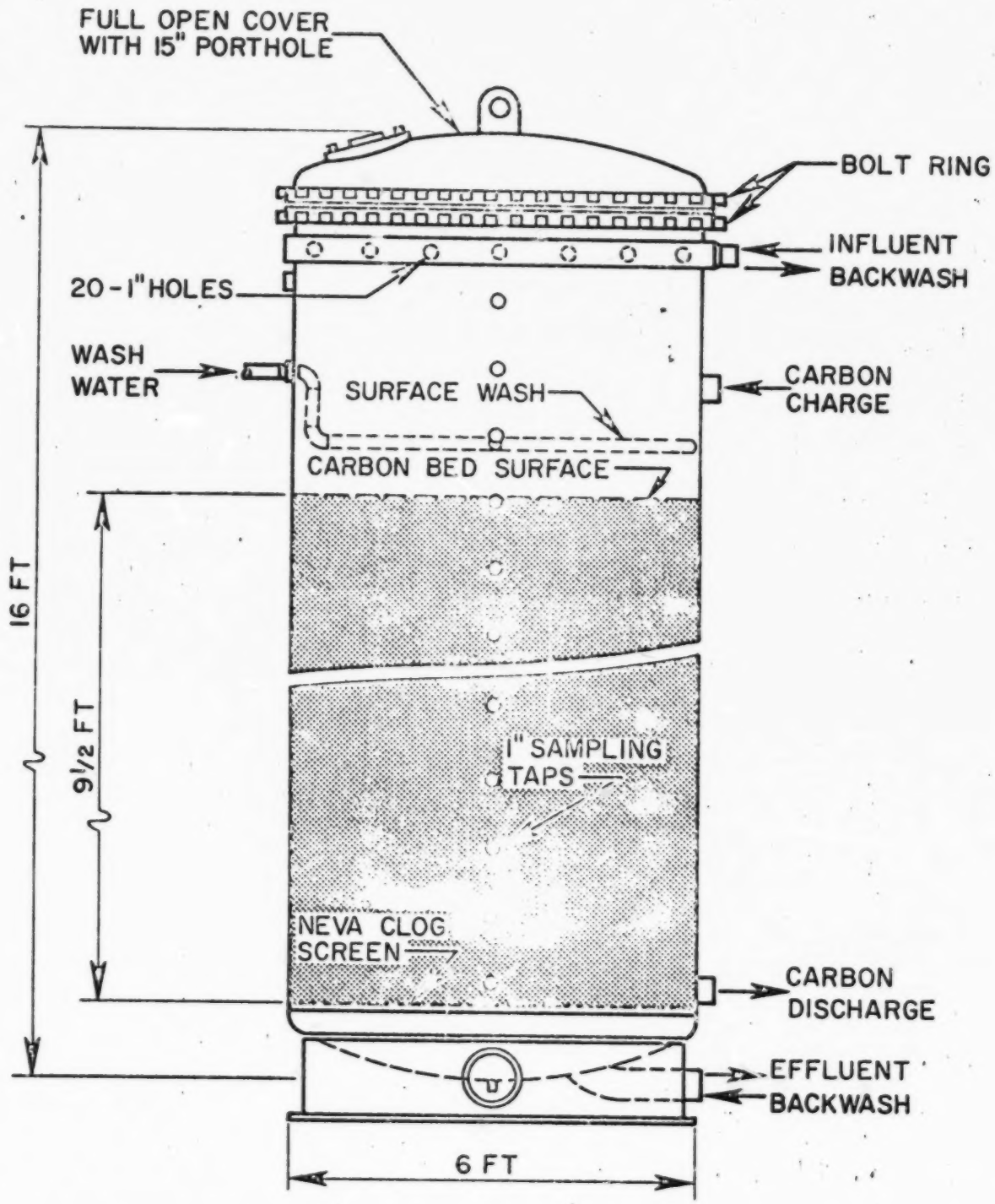

FIGURE 5. - TYPICAL CARBON CONTACTOR

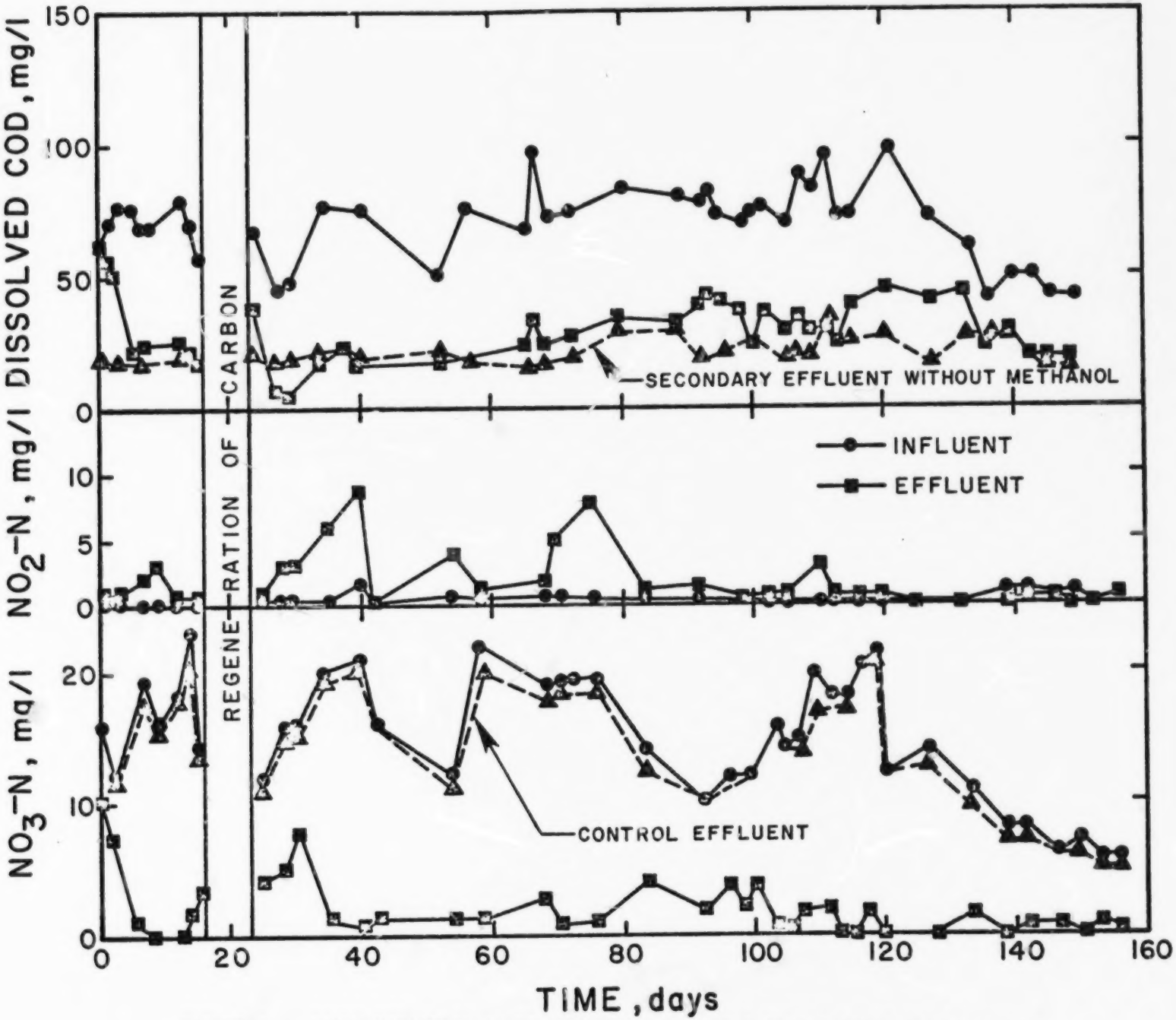

FIGURE 6. - DAILY VARIATION IN DENITRIFICATION IN THE SINGLE STAGE CARBON COLUMN

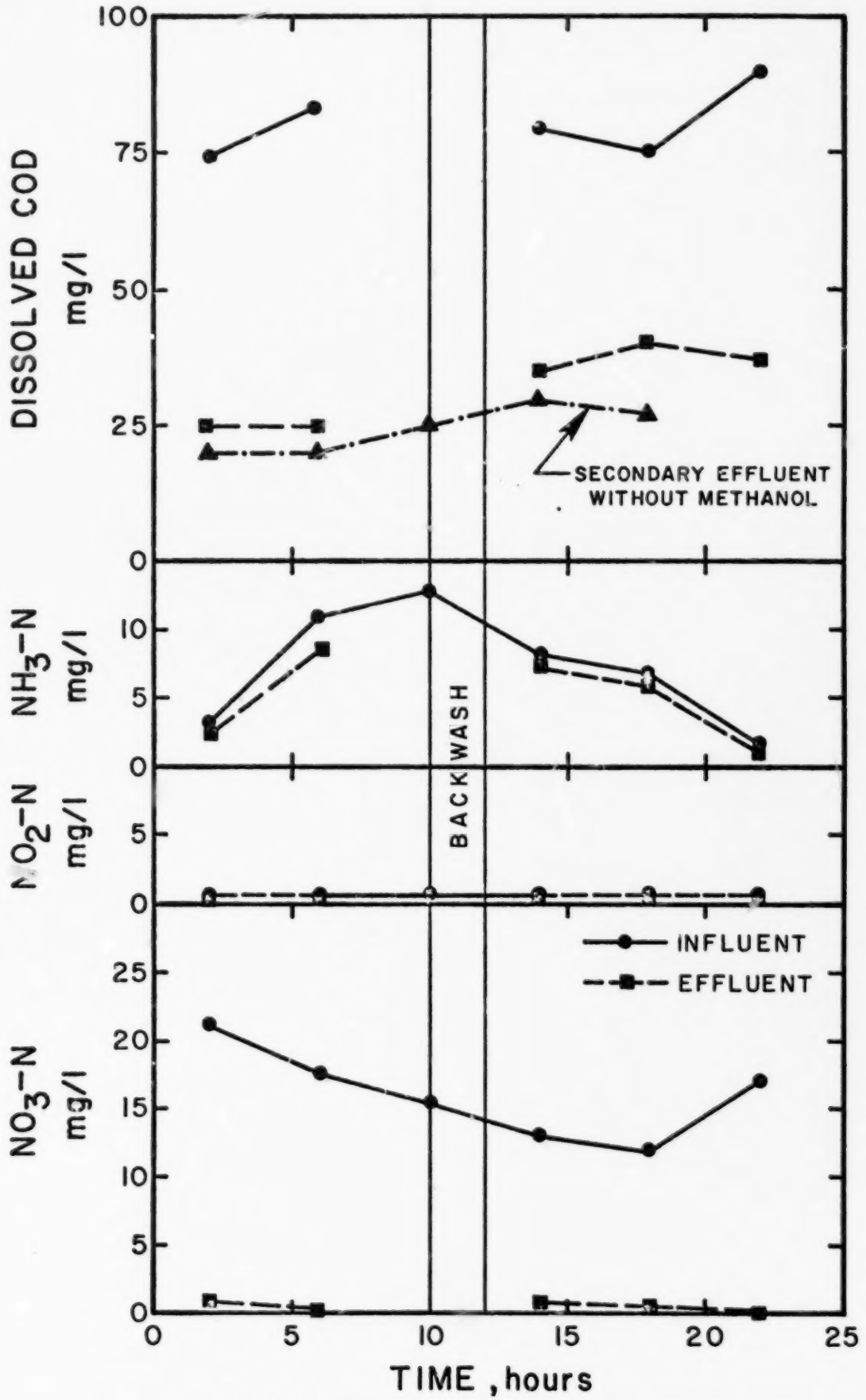

FIGURE 7. - THE EFFECT OF BACKWASHING ON DENITRIFICATION

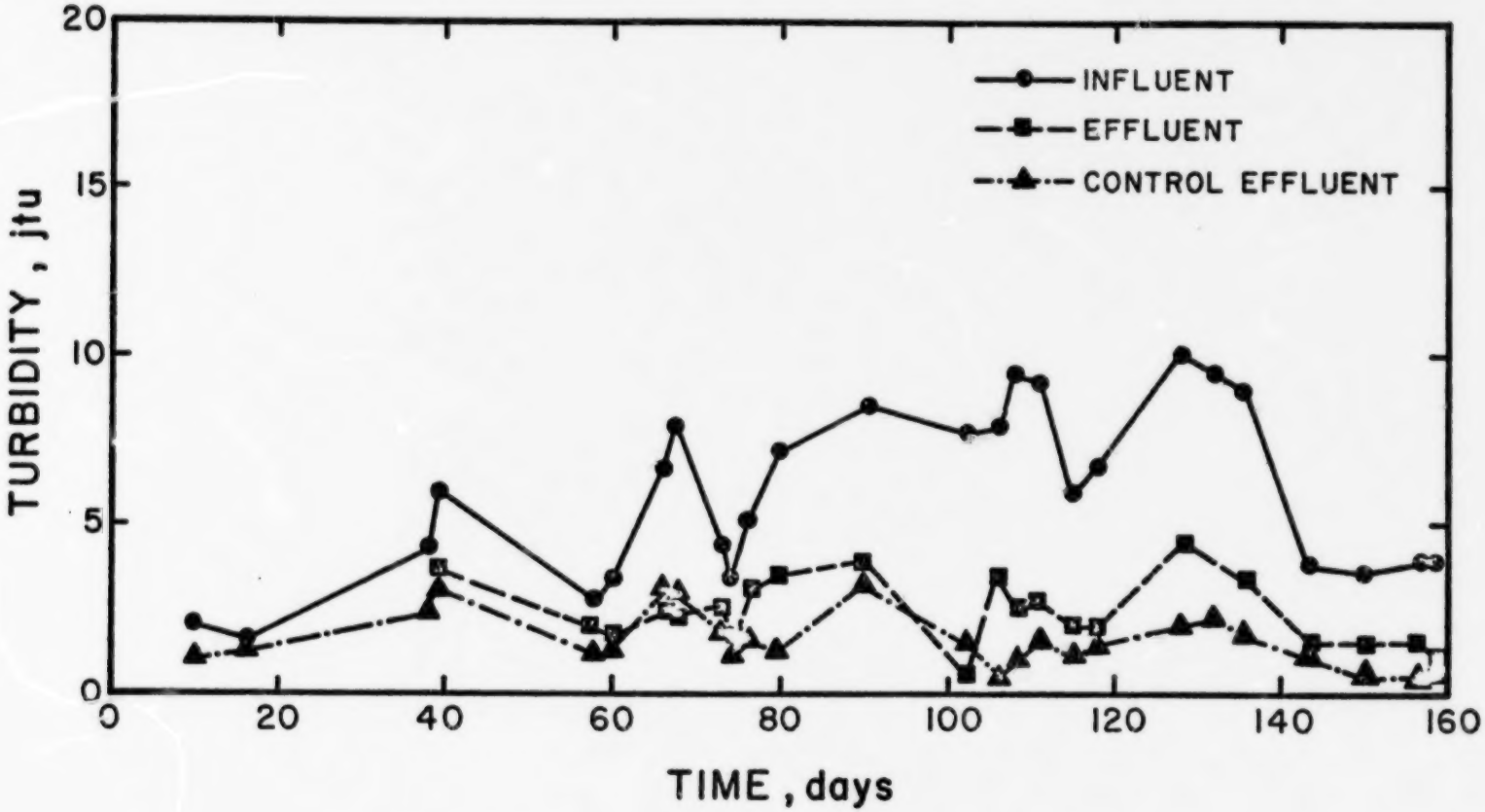

FIGURE 8. - THE EFFECT OF DENITRIFICATION ON EFFLUENT TURBIDITY

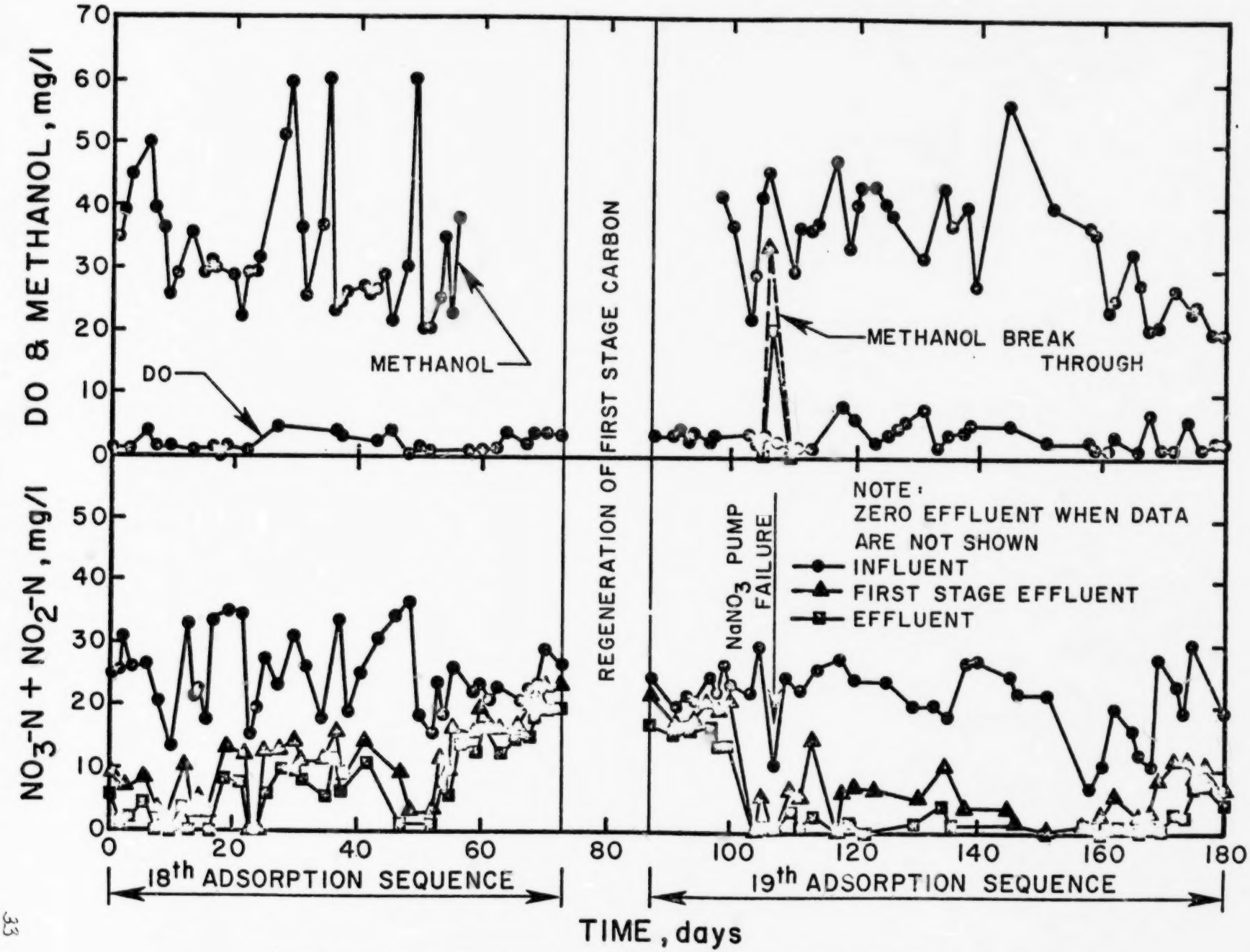

FIGURE 9. - DAILY VARIATION IN DENITRIFICATION IN THE FOUR STAGE CARBON COLUMN

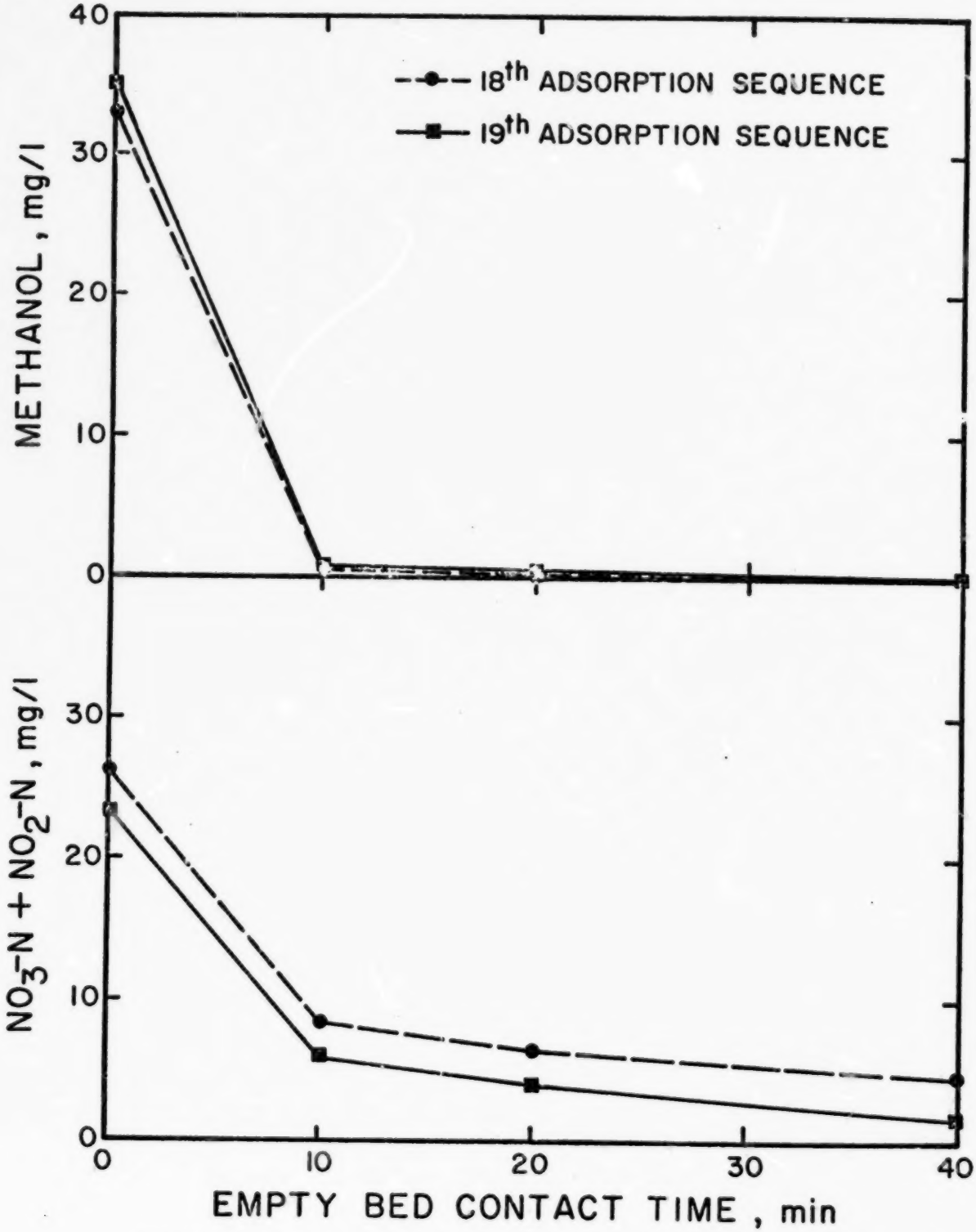

FIGURE 10. - RELATIONSHIP BETWEEN CONTACT TIME AND DENITRIFICATION IN THE FOUR STAGE CARBON COLUMN

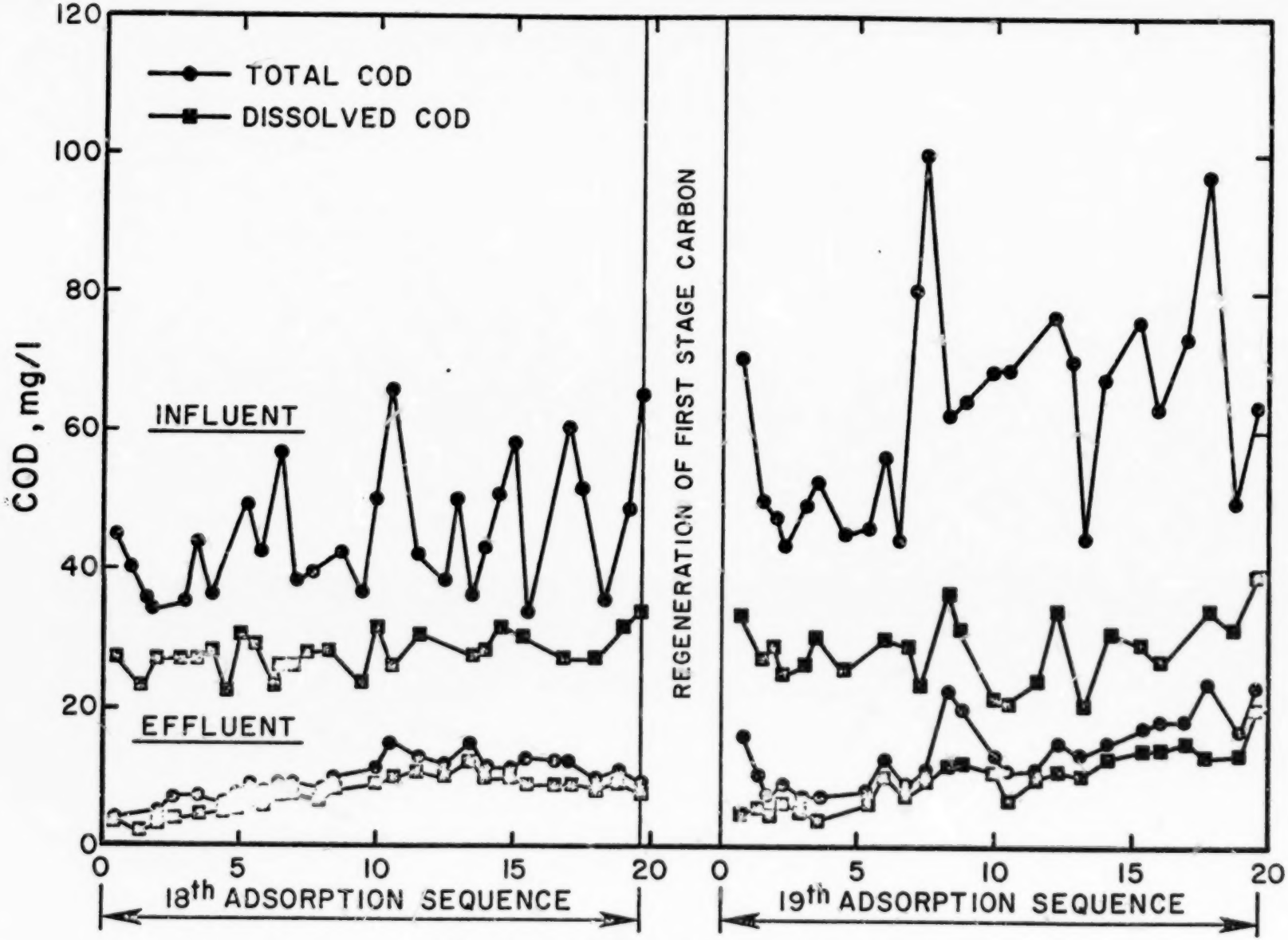

FIGURE 11. - EFFECT OF DENITRIFICATION ON COD REMOVAL IN THE FOUR STAGE CARBON COLUMN (Mil Gal x 3785 = cu m)

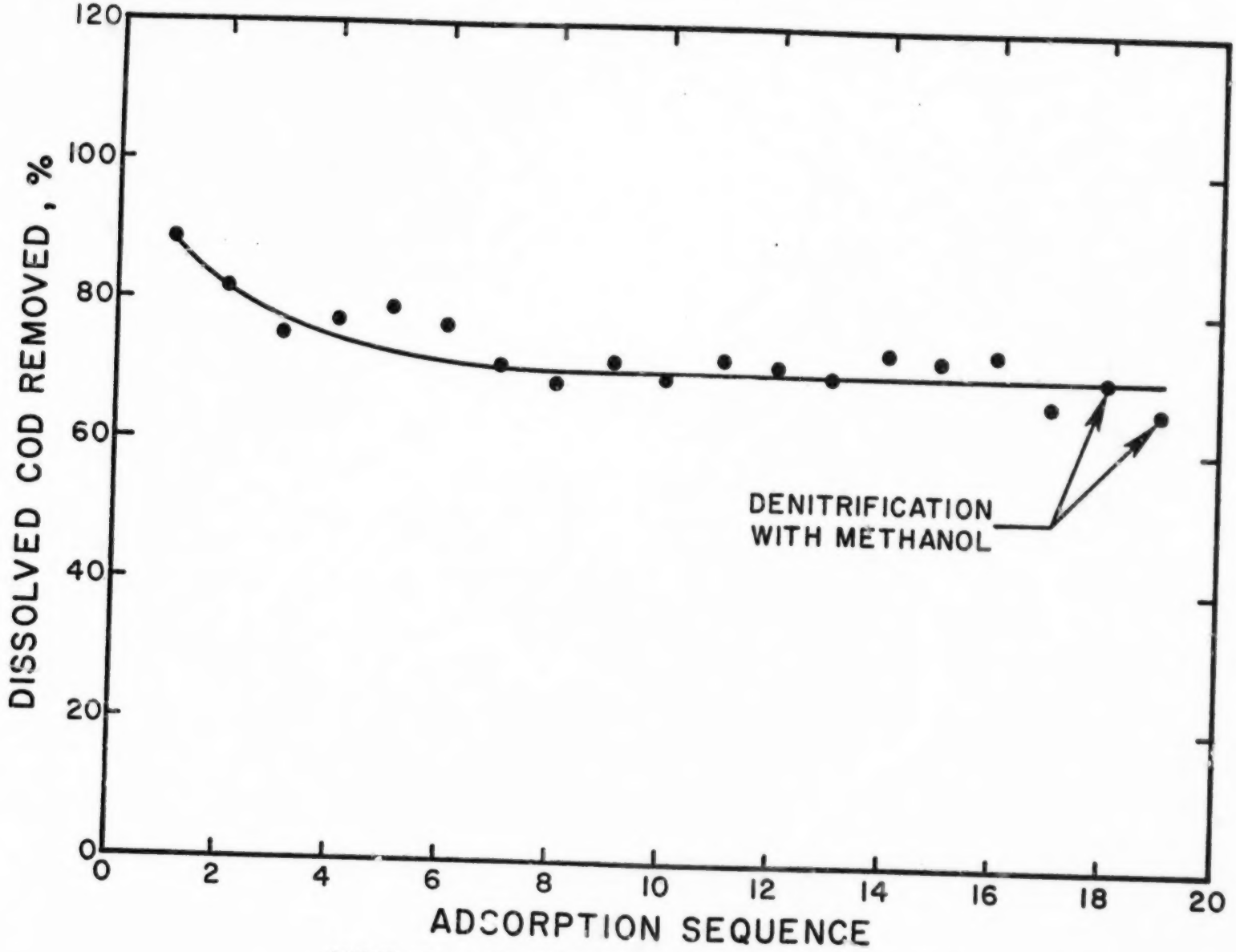

FIGURE 12. - COMPARISON OF COD REMOVAL IN THE FOUR STAGE CARBON COLUMN WITH AND WITHOUT COMBINED DENITRIFICATION

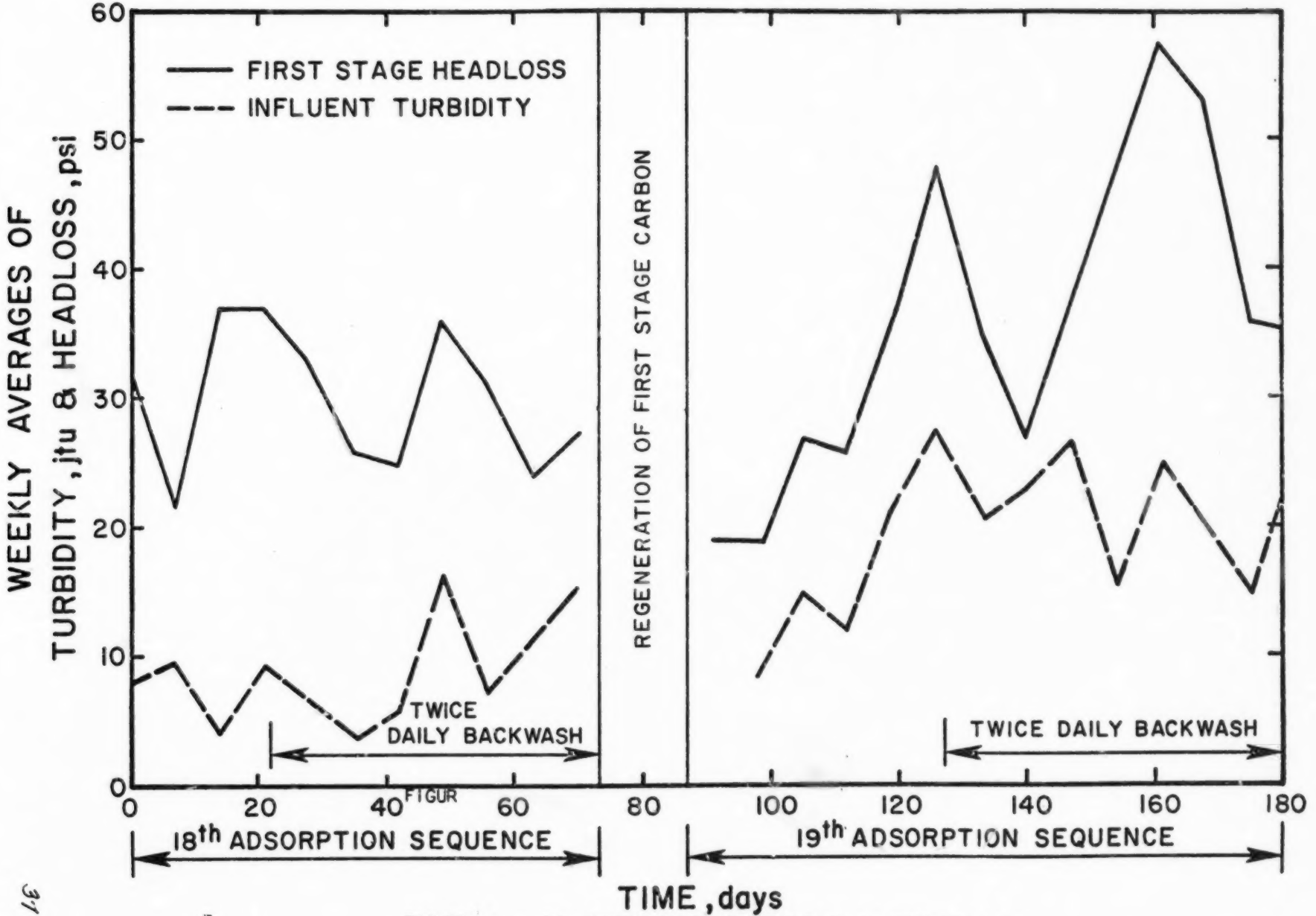

FIGURE 13. - THE EFFECT OF DENITRIFICATION ON PRESSURE LOSS IN THE FIRST STAGE CARBON (psi x 0.0703 = kg/sq. cm)

TABLE I. - VIRGIN CARBON CHARACTERISTICS

PARAMETER	VALUE
IODINE NO., mg/l	1100
METHYLENE BLUE NO., mg/g	300
MOLASSES NO.	220
APPARENT DENSITY, g/ml	0.47
ASH CONTENT, %	5
MEAN PARTICLE DIA., mm	0.90
MESH SIZE	16x40

TABLE 11. - BACTERIOLOGICAL DATA FOR FOUR STAGE COLUMN

SAMPLING POINT	COLIFORM	FECAL COLIFORM	TOTAL PLATE COUNT	PSEUDOMONAS
	MPN PER 1000 ml (x 1000)		NUMBER PER ml (x 1000)	
INFLUENT	529	79	534	391
STAGE I MIDWAY	305	84	382	279
STAGE I EFFLUENT	293	79	332	201
STAGE 2 EFFLUENT	106	44	112	59
STAGE 3 EFFLUENT	120	30	27.6	18.1
EFFLUENT	35.8	25.4	25.4	20.0

TABLE III. - COMPARISON OF CARBON CHARACTERISTICS WITH AND WITHOUT COMBINED DENITRIFICATION

PARAMETER	CARBON			
	SPENT		REGENERATED	
	17th SEQUENCE	DENITRIFICATION 18th SEQUENCE	17th SEQUENCE	DENITRIFICATION 18th SEQUENCE
IODINE NO., mg/g	409	393	649	628
METHYLENE BLUE NO., mg/g	147	146	178	160
MOLASSES NO.	118	149	203	180
ASH, %	10.7	11.4	11.6	12.6
APPARENT DENSITY, g/ml	0.648	0.633	0.550	0.544
MEAN PARTICLE DIA., mm	0.79	0.88	0.82	0.89

TABLE IV. - COST ESTIMATES FOR DENITRIFICATION
COMBINED WITH CARBON AND IN SAND COLUMNS

COST ITEM	COST $/MIL GAL		
	REMOVAL OF ORGANICS	DENITRIFICATION	
	CARBON	CARBON	SAND
CAPITAL AMORTIZATION (20 YEARS @ 5 %)	41	1	15
OPERATION AND MAINTENANCE	45	9	31
METHANOL (REMOVAL OF 20 mg/l NO_3-N)	—	15	15
TOTAL	86	25	61
COMBINED COST FOR REMOVAL OF ORGANICS AND NO_3-N	111		—

NOTE: MIL GAL x 3785 = cu m